

**Comparative study of naphthalene adsorption on activated carbon
prepared by microwave-assisted synthesis from different typical coals in
Xinjiang**

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Abstract:

Coal-based activated carbons (CACs) prepared from anthracite (A) coal, bituminous (B) coal, and long flame (L) coal (i.e., ACAC, BCAC, and LCAC) from Xinjiang, China, using KOH as activating reagent, were investigated under various microwave radiation power levels. The results show that the adsorption capacity of the obtained activated carbons (prepared under the optimum power level) towards naphthalene follows the order: ACAC > BCAC > LCAC. In addition, the textural properties of the CACs were investigated by means of SEM and low-temperature N₂ adsorption. The surface chemistry features of the CACs were investigated by XPS, FTIR spectroscopy and Boehm's titration method. ACAC has a higher surface area, pore volume, and zero point charge (pH_{PZC}) than the BCAC and LCAC, while acidic oxygen functional group of the ACAC is lower than that of BCAC and LCAC. In addition, the adsorption of naphthalene from the aqueous solution on the CACs could be favorably described by the Freundlich isotherm. The adsorption kinetics fits very well to the pseudo-second-order model. Among the three coals, A-coal was the best material having low ash content and less than 10% volatile content, which is beneficial for the preparation of CAC using microwave -assisted synthesis for naphthalene adsorption.

Keywords: Microwave radiation; Activated carbons; Adsorption; Naphthalene

1. Introduction

Activated carbon (AC), which is a crude form of graphite carbonaceous adsorbents is known for its high porous surface area, controllable pore structure, and low acid or base reactivity, making it widely used as a gas-phase and liquid-phase adsorbent [1]. One of the main challenges in the commercial manufacture of AC is to identify new precursors that are cheap, accessible and available in abundant quantities. Such precursors would have a potential for significant economic benefits. Many raw lignocellulosic materials such as rice husk [2], Jatropha hull [3], pistachio nut shells [4], cassava peel [5], bamboo [6], bean pods [7] and wood [1] have been used for the preparation of AC and have had different degrees of success over the years. However, some of these raw materials are difficult to collect and have an unstable source. Recently, coals (being the first known precursor for AC) have become again popular as raw materials for the production of AC because of their not very high price and wide prevalence [8].

Among all provinces in China, Xinjiang province has the largest coal-producing area, the coals from which have different properties. The production of coal enormously increased, exceeding 1.6 million tons in 2013. Thus, the selection of coal as a stable alternative material for the preparation of AC in Xinjiang is significant.

The preparation of AC generally involves physical or chemical activation methods under high temperature by heating [5, 6]. Conventional electric furnace heating is the common method for AC production, and this method usually takes several hours and does not ensure a uniform temperature for various sizes and shapes of samples. In recent years, microwave radiation has emerged as a promising alternative method to heat materials. Microwave

heating has been increasingly utilized in various technological and scientific fields for a variety of applications, because of its advantages; microwave heating affords faster and uniform heating rate and readily transforms to heat inside the particles by dipole rotation and ionic conduction as compared with conventional heating method [9, 10]. Nevertheless, according to the literature, information is lacking on preparation of AC from different kinds of coal under microwave radiation.

Polycyclic aromatic hydrocarbons (PAHs) always occur in oil, coal and tar deposits. In addition, the compounds are formed from the incomplete combustion of carbon-containing fuels, which are the most widespread organic pollutants. PAHs in the environment are found primarily in soil, sediment and oily substances. These compounds can enter water bodies through atmospheric deposition, urban runoff and sewage discharges. As a class of environmental pollutants, PAHs are a problem because some have been identified as carcinogenic, mutagenic and teratogenic [11]. Currently, various methods have been used to remove PAHs in water; these methods include adsorption, biodegradation and sonication [12, 13]. Moreover, adsorption has proved to be one of the most attractive techniques for removing PAHs using AC from aqueous solutions. Cabal et al. [7] studied the adsorption of naphthalene onto bean pod-derived carbons and found that carbon composition that includes mineral matter might play an important role in naphthalene retention. Yuan et al. [14] prepared a series of porous carbons and used them for PAHs adsorption, and results of experiments showed that the equilibrium data fit the non-linear Freundlich equation well and the adsorption of PAHs appeared to be a two-stage process controlled by diffusive transport processes. Iovino P et al. [15] studied single and competitive adsorption of toluene

and naphthalene onto activated carbon was fitted the Freundlich equation well. Thus, the preparation of coal-based activated carbons (CACs) from suitable types of coal in Xinjiang by microwave induction and their application in naphthalene adsorption from aqueous solution are important.

The main objectives of this study were to prepare AC from coals by microwave radiation and to evaluate the feasibility of using the produced AC to remove PAHs from aqueous solutions. Three kinds of typical Xinjiang coals (anthracite (A)-coal, bituminous (B)-coal and long flame (L)-coal) with KOH as activator were used to prepare AC. The influence of microwave power on the adsorption capacities of the CACs for naphthalene was investigated, enabling the process conditions for preparing CACs with high adsorption properties to be determined. In addition, the relationship between some properties including the BET surface area, pore volume, pH_{PZC} and surface groups, as well as the structures of CACs were investigated. Naphthalene, which is one of the most abundant PAHs in wastewater, was chosen as the target pollutant.

2. Experimental

2.1. Raw materials

These raw coals (A-coal, B-coal and L-coal) were purchased from TBEA, Xinjiang Uygur Autonomous Region, China. The coals were crushed and sieved to 100 meshes. The resultant coals were washed four times with distilled water to remove dust and dried in an air oven at 110 °C for 4 h. After cooling, the powdered coals were stored in a glass jar at room temperature. All reagents used were of analytical grade. The proximate analysis of coal was determined by standard test method (GB/T 212-2008). The selected

physic-chemical properties of A-coal, B-coal and L-coal are shown in Table 1.

Table 1 should be positioned here.

2.2. Preparation of CACs

CACs were prepared within a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. The 10 g mixture of various ratios of dried coal powder with the activator (KOH) was placed in a quartzose tube of a microwave reactor for activation under vacuum atmosphere at a given power level (300, 500, 700 and 900 W). The resulting products were washed with 10% hydrochloric acid and distilled water until the filtrate reached a neutral state. The preparation parameters of preparation for CACs from different kinds of coals were decided based on the optimum conditions reported in previous literatures [16, 17].

2.3. Characterization methods

Elemental analysis of carbon, hydrogen and nitrogen was carried out using a VarioEL III analyzer. Sulfur content was determined by Eshka method (GB/T 214-2007). The ash content was determined according to proximate analysis of coal (GB/T 212-2008) and the standard test method for granular activated carbon. The oxygen content was determined by difference.

The XPS analysis was conducted using a PHI5700 ESCA system equipped with a Mg K_{α} X-ray source (1253.6 eV) under a vacuum pressure $< 10^{-6}$ Pa. Pass energy was set as 187.85 and 29.35 eV for the survey and high-resolution spectra, respectively. The XPS spectra of the CACs were calibrated by taking the graphitic peak as 284.6 eV.

The surface morphology of the CACs was examined using scanning electron microscopy

(SEM) (JSM-6490LV, Japan) at accelerating voltages of 15 KV. Before observation, the CACs were coated with gold in E-1010 Ion sputter.

The textural properties of the CACs were characterized by N₂ adsorption at 77 K using a surface area analyzer (Micromeritics, ASAP-2020, USA), and the surface areas (S_{BET}) of CACs were calculated from the isotherms using the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V_t) was calculated by converting the adsorption amount at $P/P_0 = 0.95$ to a volume of liquid adsorbate. The external area (A_a), micropore area (A_m) and volume (V_m) were obtained using the t-plot method.

Different CACs samples were also analyzed with Fourier transform infrared spectrometer (Magna-IR 750), the samples were mixed with KBr powder and the mixtures were press into pellet. The spectra were recorded from 4000 to 400 cm⁻¹. The spectra were obtained with a resolution of 1 cm⁻¹, 10 scans per spectrum are used in FTIR measurements.

The pH_{pzc} of CACs was determined by a mass titration method proposed by Noh and Schwarz [18], which is defined as the pH of the mixtures at which surface charge density on the adsorbent is zero. CAC (0.1 g) was added to 50 mL of 0.01 mol/L NaCl solutions, then, the pH had been adjusted to a set value between 2 and 12 with NaOH or HCl. The flasks were sealed and placed on a shaker for 48 h. The pH_{pzc} is the point where $\text{pH}_{\text{final}} - \text{pH}_{\text{initial}} = 0$.

The study of the surface functional groups was based on the Boehm titration method [19]. The basic groups were neutralized with HCl solution (0.05 mol L⁻¹). The various acidic groups were determined under two assumptions, as follow: NaHCO₃ neutralized carboxyl

groups, NaOH neutralized carboxyl, lactone and phenolic groups and Na₂CO₃ neutralized carboxyl and lactone groups. An amount of 1.0 g of CAC was added to the 25.00 mL solution of one of the three 0.05 M reaction bases (NaHCO₃, Na₂CO₃ and NaOH). The solutions were then sealed and placed in a shaker for 48 h at 30 °C.

2.4. Adsorption studies

2.4.1. Adsorption performance analysis

Given the low solubility of PAHs in water, the use of ethanol as co-solvent was efficient for the solubilization of the naphthalene in the aqueous medium. Naphthalene was initially solved into ethanol aqueous solution (30 vol%) to prepare the stock solutions. The concentrations of adsorbate solutions were measured by a UV-75N spectrophotometer at $\lambda_{\text{max}} = 218 \text{ nm}$.

For the adsorption experiment, 100 mL of the 30 mg L⁻¹ naphthalene solution was placed in a 250 mL conical flask. 15 mg of CAC prepared was added into the solution. The solution was then shaken for 60 min at 20 °C. The amount of the adsorbate (Q_e) was calculated as follow:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg L⁻¹) and C_e (mg L⁻¹) are liquid-phase concentrations of naphthalene at initial and equilibrium, respectively. V (mL) represents the volume of the solution and m (g) stands for the mass of CAC used.

2.4.2. Adsorption kinetics

In the adsorption kinetic experiments, 100 mL of the 30 mg L⁻¹ naphthalene solution containing 15 mg of the CAC was placed in 250 mL conical flask. The solution was then

shaken for various times at 20 °C.

The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied for analyzing the experimental data.

The pseudo-first-order kinetic rate equation is expressed as [20]:

$$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{k_1}{Q_e t} \quad (2)$$

where k_1 is the rate constant of pseudo-first-order sorption (min), which can be determined from the slope of the linearized pseudo-first-order rate equation, Q_e and Q_t (mg g⁻¹) are the adsorption capacities at equilibrium and time t , respectively.

The pseudo-second-order kinetic rate equation is expressed as [20]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where k_2 is the second-order rate constant (g mg⁻¹ min⁻¹) can be determined from the intercept of the linearized pseudo-second-order rate equation.

In the intraparticle diffusion model, the relationship between the adsorption capacity at time t , Q_t and $t^{1/2}$ could be written as [20]:

$$Q_t = K_p t^{1/2} + C \quad (4)$$

where K_p is the intraparticle diffusion constant (mg g⁻¹ min^{-1/2}) and C is the intercept of the line, which is proportional to the boundary layer thickness.

2.4.3. Adsorption isotherm

For the adsorption isotherms experiments, 15 mg CAC and 100 mL various initial concentration of naphthalene solution (20-70 mg L⁻¹) were placed in a set of 250 mL conical flasks. Then the solution was shaken for 60 min at 20 °C.

The Langmuir adsorption Eq. (5), predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [11].

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

where C_e and Q_e are as defined in Eq. (1), q_m is adsorption maximum (mg g^{-1}); K_L is sorption equilibrium constant (L mg^{-1}).

The Freundlich isotherm [11] is an empirical equation employed to describe heterogeneous systems, and is expressed by the following Eq. (6):

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (6)$$

where K_F is a constant which represents a measure of the adsorption capacity of the adsorbent for specific solute, and n is a measure of intensity of adsorption.

The Temkin model considers the effects of some indirect adsorbent-adsorbate interactions on an adsorption isotherm, because of these interactions, the heats in adsorption would more often decrease than increase with increasing coverage [21]. This equation has the form:

$$Q_e = B \ln C_e + B \ln a \quad (7)$$

where the term B corresponds to RT/b , T is absolute temperature (K), R is the gas constant (L g^{-1}), b is the Temkin constant related to the heat of sorption (kJ mol^{-1}), and C_e is the equilibrium concentration (mg L^{-1}).

3. Results and discussion

3.1. Effect of microwave power on naphthalene adsorption on CACs

The CACs were prepared with a coal alkali ratio of 1:2 at a radiation time of 10 min.

When the microwave power was at 300 W, the pore structures had not adequately developed, and the adsorption amount was small, however, the adsorption capacity showed a drastic increase with the increase of microwave power (Fig. 1); such a phenomenon could be ascribed to the combined effect of internal and volumetric heating, which expanded the carbon structure [22]. However, if microwave power is higher than 700 W, over-gasification might cause the destruction of pore structures, thereby progressively decreasing adsorption capability. Moreover, exorbitant temperatures might produce local hotspots, leading to external ablation, shrinkage and collapse of the carbon framework, and consequently reducing the accessibility of active sites. Therefore, the microwave power levels proposed were at 500 and 700 W for the effective activation of the ACAC (LCAC) and BCAC, respectively. Porosity development may depend on ash. Indeed, mineral matter is known to act as a catalyst to accelerate gasification reactions during activation processes [23]. Furthermore, the release of volatile matter favors porosity development. The adsorption amounts of naphthalene on the CACs prepared under the optimum power level followed the order: ACAC > BCAC > LCAC. This result may be due to the fact that A-coal has lower contents of volatile matter and ash than B-coal and L-coal [24]. Thus, A-coal is a more suitable raw material for CACs production than B-coal and L-coal.

Fig. 1 should be positioned here.

3.2. Characterization of CACs

3.2.1. Element contents analysis

According to the results, the three CACs had similar elemental compositions (Table 1). The carbon content of the CACs pronouncedly increased after activation. On the contrary,

the oxygen content was decreased in CACs. Meanwhile, the C/O ratios increased from 2.81, 2.49, 2.39 for the A-coal, B-coal and L-coal to 4.58, 4.42 and 4.26 for the ACAC, BCAC, LCAC, respectively, this could be due to some oxygen-containing groups were eliminated from the carbon surface. Meanwhile, the content of nitrogen and sulfur also had a certain decrease.

3.2.2. XPS analysis

The survey spectra of the CACs contained distinct peaks for carbon and oxygen and weak peaks for nitrogen (Fig. 2). It can be seen that the C content increased while the contents of O decreased after microwave treatment, implying the elimination of the oxygen groups of CACs during the activation process.

Fig. 2 should be positioned here.

3.2.3. Surface morphology

SEM images of the coals and CACs are shown in Fig. 3. It showed that the surfaces of the coals are fairly smooth without any pores. After activation, the external surfaces of the three CACs exhibited a highly pronounced and almost irregular pore structure. Reaction (1) to result in the widening the existing pores by the internal structure of carbon matrix and to create new porosities [25], as follows:

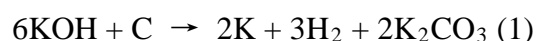


Fig. 3 should be positioned here.

3.2.4. Textural structure

The isotherms demonstrated a sharp rise at the low P/P_0 range, and a gradual increase at the relatively high P/P_0 range (Fig. 4). According to the IUPAC classification system, all

the adsorption isotherms belonged to type I, thereby indicating that all the CACs were mainly micropores. The desorption branch presents a small hysteresis loop at high relative pressures, thereby indicating the presence of mesoporosity. This adsorption behavior suggests a combination of microporous-mesoporous structure. Among the samples, the ACAC showed the best developed porosity. Such porous features may be ideally adapted for the removal of aromatics from an aqueous phase. The BET surface area and pore volume of the ACAC were evaluated as $1450.28 \text{ m}^2 \text{ g}^{-1}$ and $0.66 \text{ cm}^3 \text{ g}^{-1}$, respectively (Table 2), which are both larger than those of BCAC and LCAC. This finding may be due to the high ash levels of B-coal and L-coal (Table 1), given that ashes do not contribute to porosity, high ash levels in the precursor naturally lead to reduced pore volumes [24]. In addition, when a small amount of volatile overflows, the left pore channels play an important role in the activation process, which obviously promotes pore development of CACs, however, highly volatile coal will lead to agglomeration during carbonization, and a large amount of volatile gas discharge increases the processing load, generally, less than 10% of the volatile matter is beneficial [26]. And these are directly related to its adsorptive capacity, which is corresponding with the previous adsorption results.

Fig. 4 should be positioned here.

Table 2 should be positioned here.

3.2.5. Surface chemistry features of CACs

ACAC has a higher pH_{PZC} value and more basic groups than BCAC and LCAC (Table 3). Moreover, ACAC has less number of acidic functional groups than BACA and LCAC. These results could be due to the different physical properties of the raw coals. Furthermore, ACAC achieved the largest naphthalene adsorption amount among the CACs. It could be

concluded the decrease of acid oxygen-containing functional groups and the increase of basic groups in the ACAC could enhance the adsorption amount of naphthalene.

Table 3 should be positioned here.

3.2.6. FTIR spectra of CACs

The three CACs showed similar FTIR spectra (Supporting information Fig. S1), indicating that they have identical species of functional groups on the surface. The broad band at approximately 3450 cm^{-1} is assigned to the O-H stretching vibration of the hydroxyl functional groups, including hydrogen bonding [27]. The peak is less pronounced in the ACAC sample than in the other samples, implying the presence of a lower number of -OH groups in the carboxylic groups of ACAC than in those of BCAC and LCAC. As observed among the samples, ACAC had the lowest number of acid oxygen-containing functional groups. The minimal acidic oxygen functional groups such as phenols and carboxyls of the CACs may enhance the adsorption capacity of naphthalene from the aqueous solution, as shown in the results of the acid-base titration.

3.3. Adsorption kinetics of naphthalene on CACs

The adsorption kinetics of naphthalene is shown in Fig. 5. The kinetic models of pseudo-first-order, pseudo-second-order, and intraparticle diffusion were tested to correlate the experimental kinetic data of naphthalene on the three CACs (Table 4). The three CACs appeared to have similar behaviors in terms of kinetics. The adsorption process has two stages: at the first stage, naphthalene is rapidly adsorbed onto the easily accessible hydrophobic sites within the first 20-min period. At the second stage, the uptake is probably limited by the slower migration of naphthalene to less accessible sites associated with mesopores, thus taking a longer adsorption time. Yuan et al. [14] reported similarly

that the adsorption process of PAHs onto petroleum coke-derived porous carbon also was the two-stage. In addition, the adsorption rate constants of ACAC determined are higher than that of BCAC and LCAC. This is due to that ACAC has higher surface area, more abundant sorption sites and superior distribution of pore sizes than BCAC and LCAC (Table 2 and Fig. 4). An ideal percentage of pores of ACAC in the mesopore and macropore (20–500 Å) size ranges could be minimized the kinetic diffusion resistance during the adsorption process [28].

The pseudo-second-order model had higher R^2 and Q_{exp} values that were closer to the experimental values than the pseudo-first-order and intraparticle diffusion models. The pseudo-second-order model demonstrated better fitting for all three CACs than the others. Cabal et al. [7] also found the experimental data of adsorption kinetics of aqueous naphthalene on the AC from bean pods were fitted to the pseudo-second kinetic model well. The adsorption mechanism and the potential rate-determining steps of naphthalene on CACs could be involved in mass transport and chemical reaction processes [21]. In addition, ACAC has higher mesopore volume, which is supported that intraparticle diffusion could be involved in the sorption process of naphthalene on CACs. However, it was not the only rate-determining step.

Fig. 5 should be positioned here.

Table 4 should be positioned here.

3.4. Adsorption isotherm of CACs

The adsorption isotherms of naphthalene from the solution on CACs are depicted in Fig. S2 (Supporting information). Table 5 lists the parameters of the Langmuir, Freundlich and Temkin adsorption isotherm models of naphthalene on three CACs at 20 °C, along with

their regression coefficients (R^2). Compared with Langmuir and Temkin, the equilibrium data was well represented by the Freundlich equation. Similarly, Yuan et al. [14] reported that the equilibrium adsorption isotherms of naphthalene from water on petroleum coke-derived porous carbon was fitted the Freundlich equation well. This indicates that the adsorption of naphthalene onto CACs is heterogeneous and may not be confined to a monolayer adsorption. As shown in Table 5, “ $1/n$ ” values are between 0.1 and 1, thereby indicating a favorable adsorption [21]. Since naphthalene is nonpolar compounds, this observation indicates a strong hydrophobic interaction between the CAC and naphthalene with a favorable adsorption [16].

Table 5 should be positioned here.

3.5. Effect of CACs’ surface characteristics on naphthalene adsorption

The adsorption amount of the adsorbate on CACs is generally related to the CACs’ surface characteristics, texture and surface physicochemical properties. Results (Fig. S3 Supporting information) showed that obtaining a well-developed total pore volume, high surface area, low oxygen content, and a high basic functional group is necessary to improve the adsorption capacity towards naphthalene on CACs.

4. Conclusions

Three kinds of ACs were prepared from typical coals in Xinjiang using microwave radiation. Our results indicate that microwave heating is an effective method for the processes involved. The BET surface area and pore volume of ACAC (obtained at 700 W) were higher than those of BCAC and LCAC. For CACs, the presence of microporous-mesoporous structures enhanced the specific naphthalene adsorption. The FTIR spectra suggested that the CACs had similar functional groups on the surface, and that of ACAC

contained higher number of basic functional groups and higher pH_{PZC} than the other samples. The ACAC had a lower number of acid oxygen-containing groups. The results agreed with those obtained from acid-base titration. In addition, raw coal with a low content of ash and volatile matter was suitable for the preparation of ACs. For the three CACs, the Freundlich isotherm model described the equilibrium data well. The optimum adsorption capacity towards naphthalene on the ACAC was 167.01 mg g^{-1} . Moreover, the adsorption kinetics fits very well to the pseudo-second-order model. Among the three coals, anthracite coal is the best material for the preparation of CACs for naphthalene adsorption.

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References

- [1] Wang TH, Tan SX, Liang CH. Preparation and characterization of activated carbon from wood via microwave-induced ZnCl_2 activation. *Carbon* 2009; 47:1867-5.
- [2] Foo KY and Hameed BH. Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K_2CO_3 activation. *Bioresour Technol* 2011; 102:9814-7.
- [3] Duan XH, Srinivasakannan C, Peng J H, Zhang L B, Zhang ZY. Preparation of activated carbon from *Jatropha* hull with microwave heating: Optimization using response surface methodology. *Fuel Process Technol* 2011; 92:394-0.
- [4] Foo KY and Hameed BH. Preparation and characterization of activated carbon from pistachio nut shells via microwave-induced chemical activation. *Biomass Bioenerg* 2011^a; 35:3257-1.
- [5] Sudaryanto Y, Hartono SB, Irawaty W, Hindarso H, Ismadji S. High surface area activated carbon prepared from cassava peel by chemical activation. *Bioresour Technol* 2006; 97:734-9.
- [6] Liu QS, Zheng T, Wang P, Guo Liang. Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. *Ind Crop Prod* 2010; 31:233-8.
- [7] Cabal B, Budinova T, Ania CO, Tsyntsarski B, Parra JB, Petrova B. Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. *J Hazard Mater* 2009; 161:1150-6.
- [8] Duan XX, Srinivasakannan C, Qu WW, Wang X, Peng JH, Zhang LB. Regeneration of

399 microwave assisted spent activated carbon: Process optimization. adsorption isotherms
 400 and kinetics, Chem Eng Process 2012; 53:53-2.

401 [9] Ji YB, Li TH, Zhu L, Wang XX, Lin QL. Preparation of activated carbons by
 402 microwave heating KOH activation. Appl Surf Sci 2007; 254:506-2.

403 [10] Huang LH, Sun YY, Wang WL, Yue QY, Yang T. Comparative study on
 404 characterization of activated carbons prepared by microwave and conventional heating
 405 methods and application in removal of oxytetracycline (OTC). Chem Eng J 2011;
 406 171:1446-3.

407 [11] Wassenberg DM and Di Giulio RT. Synergistic embryotoxicity of polycyclic aromatic
 408 hydrocarbon aryl hydrocarbon receptor agonists with cytochrome P4501A inhibitors in
 409 *Fundulus heteroclitus*. Environ Health Persp 2004; 112:1658-4.

410 [12] Xia XH, Yu H, Yang ZF, Huang GH. Biodegradation of polycyclic aromatic
 411 hydrocarbons in the natural waters of the Yellow River: Effects of high sediment
 412 content on biodegradation. Chemosphere 2006; 65:457-6.

413 [13] Liu JJ, Wang XC, Fan B. Characteristics of PAH adsorption on inorganic particles and
 414 activated sludge I domestic wastewater treatment. Bioresour Technol 2011;
 415 102:5305-1.

416 [14] Yuan MJ, Tong ST, Zhao SQ, Jia CQ. Adsorption of polycyclic aromatic
 417 hydrocarbons from water using petroleum coke-derived porous carbon. J Hazard Mater
 418 2010; 181:1115-0.

419 [15] Iovino P, Canzano S, Capasso S, Di Natale M, Erto A, Lama A, Musmarra D. Single
 420 and competitive adsorption of toluene and naphthalene onto activated carbon. Chem
 421 Eng Transactions. 2013; 32,67-72.

422 [16] Ge XY, Tian F, Wu ZL, Yan YJ, Cravotto G, Wu ZS. Adsorption of naphthalene from

aqueous solution on coal-based activated carbon modified by microwave induction:
Microwave power effects. Chem Eng Process 2015; 91:67-7.

[17] Xiao XM, Tian F, Yan YJ, Wu ZS. Adsorption behavior of pyrene onto coal-based
activated carbon prepared by microwave activation. Journal of Shihezi University
(Natural science) 2014; 32:486-0.

[18] Noh JS and Schwarz JA. Estimation of the point of zero charge of simple oxides by
mass titration. J Colloid Interface Sci 1989; 130:157-164.

[19] Boehm HP. some aspects of the surface chemistry of carbon blacks and other carbons,
Carbon 1994; 32:759-9.

[20] Atul V, Maldhure Ekhe JD. Preparation and characterizations of microwave assisted
activated carbons from industrial waste lignin for Cu (II) sorption. Chem Eng J 2011;
168:1103-1.

[21] Vidal CB, Barros AL, Moura CP, de Lima AC, Dias FS, Vasconcellos LC, Fechine PB,
Nascimento RF. Adsorption of polycyclic aromatic hydrocarbons from aqueous
solutions by modified periodic mesoporous organosilica. J Colloid Interface Sci 2011;
357:466-3.

[22] Emamia Z and Azizianb S. Preparation of activated carbon from date sphate using
microwave irradiation and investigation of its capability for removal of dye pollutant
from aqueous media. J Anal Appl Pyrol 2014; 108:176-4.

[23] Tellez-Juárez MC, Fierro V, Zhao W, Fernández-Huerta N, Izquierdo MT, Reguera E,
Celzard A. Hydrogen storage in activated carbons produced from coals of different
ranks: Effect of oxygen content. Int J Hydrogen Energ 2014; 39:4996-2.

- [24] Cui H, Cao Yan, Pan WP. Preparation of activated carbon for mercury capture from chicken waste and coal. *J Anal Appl Pyrolysis* 2007; 80:319-4.
- [25] Ahmed MJ and Theydan SK. Optimization of microwave preparation conditions for activated carbon from Albizia lebbeck seed pods for methylene blue dye adsorption. *J Anal Appl Pyrol* 2014; 105:199-8.
- [26] Xing BL, Huang GX, Chen LJ, Zhang CX, Wang L. Preparation and characterization of high quality low-rank coal based activated carbon. *Journal of China Coal Society* 2013; 38:218-2.
- [27] Liu QS, Zheng T, Wang P, Guo L. Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. *Ind Crop Prod* 2010; 31:233-8.
- [28] Bu J, Loh G, Gwie CG, Dewiyanti S, Tasrif M, Borgna A. Desulfurization of diesel fuels by selective adsorption on activated carbons: Competitive adsorption of polycyclic aromatic sulfur heterocycles and polycyclic aromatic hydrocarbons. *Chem Eng J* 2011; 66:207-7.

Figure captions:

Fig. 1 Adsorption amount of naphthalene on the ACAC, BCAC and LCAC prepared using various microwave power levels ($C_0 = 30 \text{ mg g}^{-1}$).

Fig. 2 XPS survey spectra of raw coals and CACs.

Fig. 3 SEM micrographs of the raw coals and CACs at 5000 \times magnification.

Fig. 4 N_2 adsorption/desorption isotherms at 77 K (a) and pore size distribution (b).

(ACAC and LCAC under microwave power of 500 W and BCAC under 700 W).

Fig.5 Adsorption kinetics of naphthalene on CACs ($C_0 = 30 \text{ mg L}^{-1}$, 20 $^\circ\text{C}$).

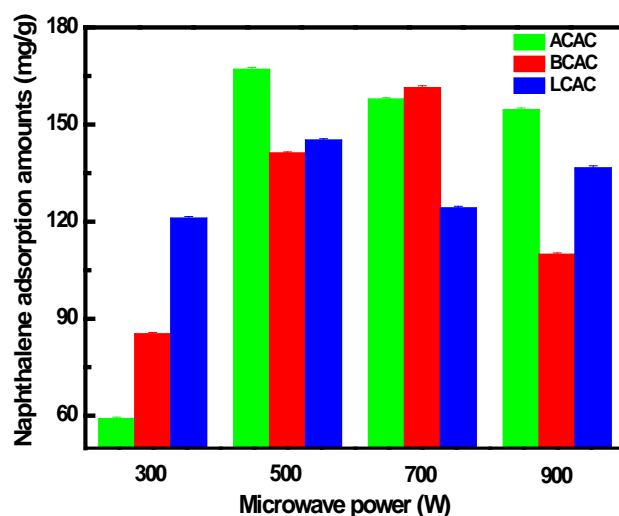


Fig.1. Adsorption amount of naphthalene on the ACAC, BCAC and LCAC prepared using various microwave power levels ($C_0 = 30 \text{ mg g}^{-1}$).

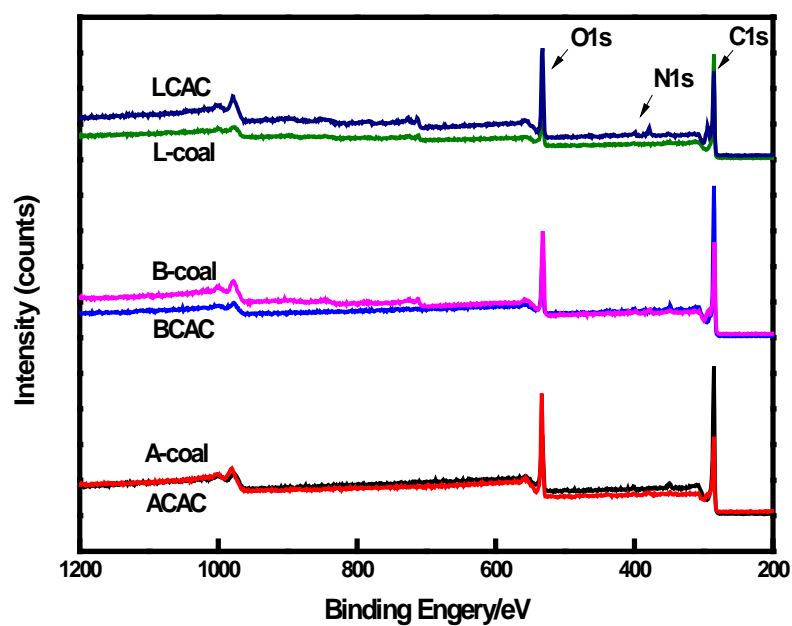


Fig. 2. XPS survey spectra of raw coals and CACs.

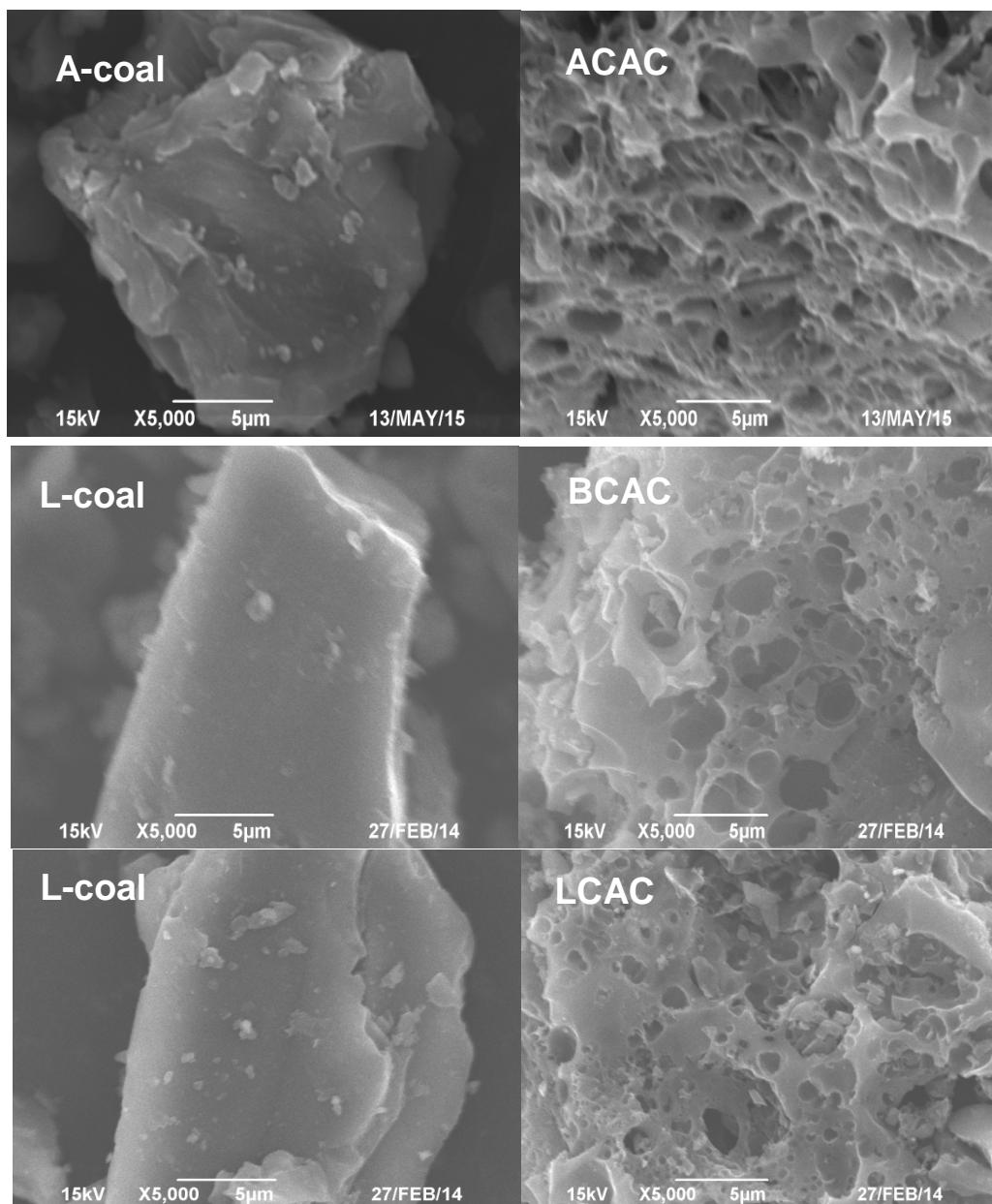


Fig. 3. SEM micrographs of the raw coals and CACs at 5000 \times magnification.

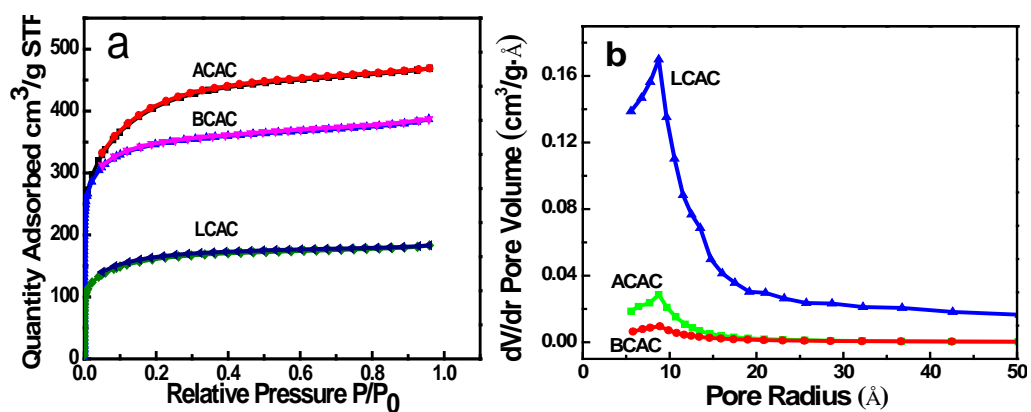


Fig.4. N_2 adsorption/desorption isotherms at 77 K (a) and pore size distribution (b).

(ACAC and LCAC by microwave power of 500 W and BCAC by 700 W)

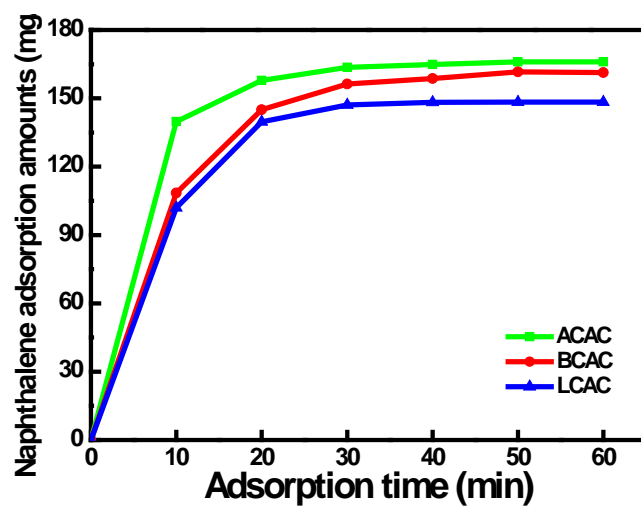


Fig. 5. Adsorption kinetics of naphthalene on CACs ($C_0 = 30 \text{ mg L}^{-1}$, 20°C).

Table 1 Characteristics of coals selected and atomic content of the coals and CACs.

Samples	Moisture %	Ash %	Volatile %	Fixed carbon %	Atom content %					
					C	H	N	S	O _{diff}	C/O
A-coal	9.00	4.21	24.98	61.81	70.75	3.18	0.68	0.25	25.14	2.81
B-coal	9.10	6.01	31.60	53.29	67.58	4.30	1.00	0.05	27.07	2.49
L-coal	2.10	6.10	38.8	53.0	66.12	5.01	1.22	0.06	27.59	2.39
ACAC	-	5.20	-	-	80.25	1.14	0.95	0.13	17.53	4.58
BCAC	-	8.01	-	-	78.68	2.23	1.21	0.08	17.80	4.42
LCAC	-	8.12	-	-	77.35	2.90	1.45	0.15	18.15	4.26

Table 2 Surface characteristics of the prepared CACs.

Samples	Microwave power W	S _{BET} (m ² g ⁻¹)	A _m (m ² g ⁻¹)	A _e (m ² g ⁻¹)	V _{mic} (cm ³ g ⁻¹)	V _{mes} (cm ³ g ⁻¹)	V _t (cm ³ g ⁻¹)	V _{mic} /V _{mes} (%)	Average pore radius (Å)
ACAC	500	1450.28	614.36	835.92	0.26	0.40	0.66	26/40	13.72
BCAC	700	1209.99	869.35	340.64	0.38	0.17	0.55	38/17	18.08
LCAC	500	570.52	337.57	232.95	0.15	0.11	0.26	15/11	15.54

S_{BET}: specific surface area obtained by BET equation, A_m, A_e: micropore area, external surface area, V_{mic}, V_{mes}, V_t: micropore volume, mesoporous volume, total pore volume.

Table 3 Surface chemistry of the CACs

Samples	Lactone (mmol g ⁻¹)	Phenolic (mmol g ⁻¹)	Carboxyl (mmol g ⁻¹)	Total acidic (mmol g ⁻¹)	Basic (mmol g ⁻¹)	pH _{PZC}
ACAC	0.4006	0.0013	0.0047	0.4066	5.1250	7.35
BCAC	0.3924	0.0307	0.0120	0.4351	4.7900	7.21
LCAC	0.3815	0.0633	0.0233	0.4681	3.9250	7.15

Table 4 kinetic model parameters for the adsorption of naphthalene on the CACs.

Samples	Q_{exp} (mg g ⁻¹)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
		k_1 (min ⁻¹)	Q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	Q_e (mg g ⁻¹)	R^2	k_p (mg g ⁻¹ min ^{1/2})	R^2
ACAC	167.01	2.3333	165.67	0.980	0.0033	166.71	0.999	8.9770	0.830
BCAC	161.36	2.2568	161.21	0.968	0.0014	161.37	0.997	4.0300	0.860
LCAC	145.15	2.0594	147.10	0.929	0.0019	144.68	0.996	8.9400	0.679

601 Table 5 Isotherm constants for the adsorption of naphthalene in aqueous solution onto the
602 CACs at 20 °C.

Samples	Langmuir			Freundlich			Temkin		
	$K_L(\text{L mg}^{-1})$	$q_m(\text{mg g}^{-1})$	R^2	$K_F(\text{L g}^{-1})$	$1/n$	R^2	B	K_t	R^2
ACAC	0.32	166.67	0.982	69.48	0.44	0.992	29.29	1.16	0.973
BCAC	0.13	156.28	0.980	32.39	0.58	0.995	26.52	0.41	0.988
LCAC	0.06	150.00	0.998	12.58	0.76	0.999	26.66	0.21	0.992

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